Next Generation Three-Way Catalysts for Future, Highly Efficient Gasoline Engines

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Ford Research and Advanced Engineering
9-June-2016

Project ID: PM067

Overview

Research and Advanced Engineering

Timeline

- Start Date: 1-Oct-2014
- End Date: 30-Sept-2017
- Status: ~ 50% complete

Budget

- Total funding: $1,690,470
  - DOE share: $752,376
  - Contractor share: $338,094
  - Additional ORNL $600,000
- Funding in FY 2015
  - $301,228 (+ ORNL $600,000)
- Funding in FY 2016
  - $257,494

Barriers

- Long lead times for materials commercialization
- Cost

Partners

- Ford Motor Company
- Oak Ridge National Lab
- University of Michigan

Relevance

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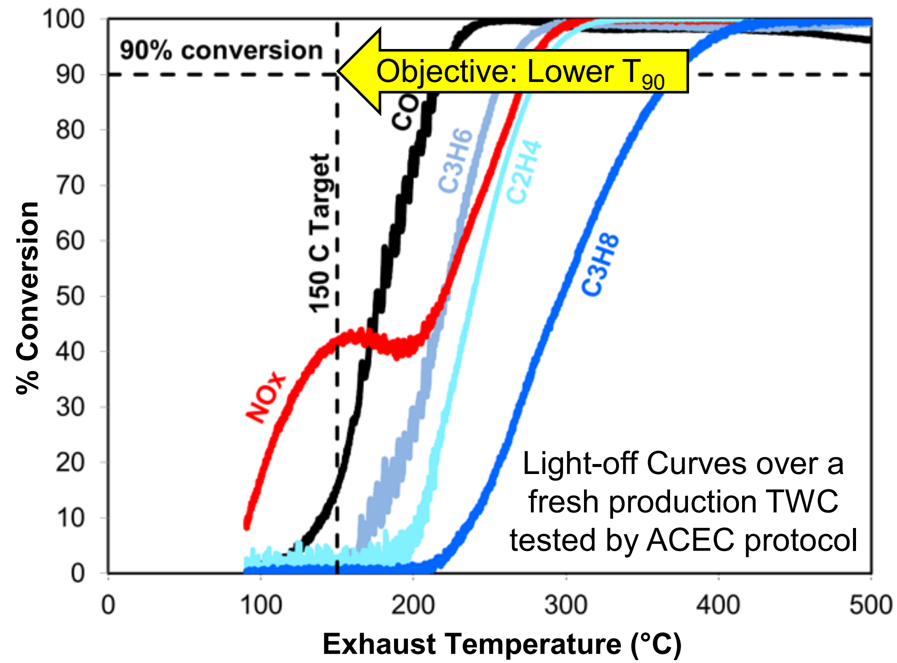
➢ Overall Objective

- Develop new three-way catalysts and/or catalyst systems capable of achieving durable 90% activity [HC, CO, NOx] at 150°C.
  - Today's automotive three-way catalysts (TWCs) become highly efficient only when exhaust temperatures reach 250-400°C.
  - The next generation of engines will be more efficient and thus produce cooler exhaust at low load conditions
  - *TWC activity will be required at lower temperatures to satisfy strict emission standards with the next generation of automobiles.*



➢ Current Budget Year Objectives

- Identify/characterize new materials, and predict performance and costs.
- Identify/capitalize on synergies between various catalyst materials within and between partners

Milestones

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Milestone	Status
Confirm Reactor Comparability • Cross lab comparisons and test protocol were confirmed	Completed Nov. 2015
Commercial vs. New Material Performance – Status (BP1) • Tested and compared commercial TWC material to new materials developed in-house	Completed Nov. 2015
Down-select Promising Materials/Confirm Synthesis and Characterization Path(s) • Agreed to keep all material synthesis pathways active through this budget period	Completed Oct. 2015
Confirm Test Protocols and Down-select Criteria • Agreed on test protocol and laboratory systems to allow cross-lab comparisons.	Completed Oct. 2015
Confirm Benchmark State of the Art TWC • Agreed no new benchmarking was necessary.	Completed Oct. 2015
Commercial vs. New Material Performance – Status (BP2) • Evaluations of new materials made in house and comparison to the commercial TWC material will continue throughout project as new materials show promise.	Ongoing
System Model Assessment – Status • New assessments will be completed as necessary.	Mar. / Jun 2016
Cost Model Assessment – Status • New assessments will be completed as necessary.	Sept. 2016
Down-Select Promising Catalysts • Determine which catalysts and/or catalyst materials should be carried over into Budget Period 3.	Sept. 2016

Approach/Strategy

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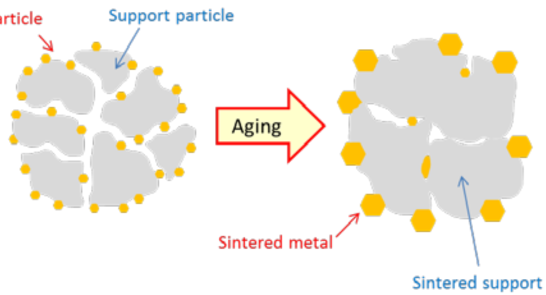
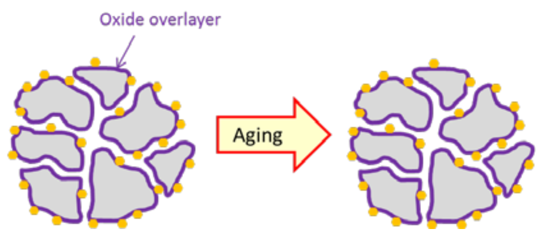
- Identify strategies to improve precious metal dispersion and promote activity
- Make and characterize new materials, and predict performance and costs
- Leverage cross-laboratory analytical capabilities

Oxide overlayer on oxide support

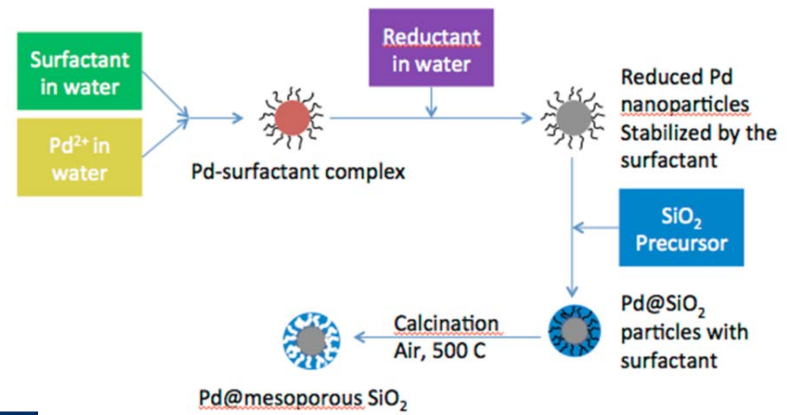
Challenge:
Prolonged exposure to high temperature automotive exhaust gases leads to sintering of both active metal and support, leading to loss of activity



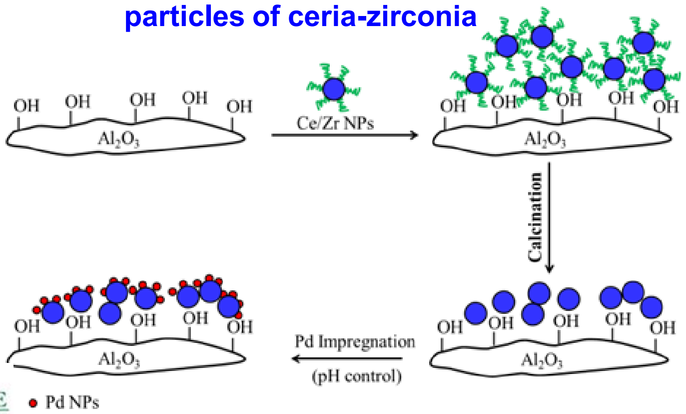
Approach:
Overcoat a high surface area oxide with a second oxide layer to reduce sintering and promote precious metal activity



One-pot synthesis of $Pd@SiO_2$ core-shell catalyst



Improved dispersion and enhanced low temperature activity on using nanophase particles of ceria-zirconia



Partnerships

Ford Motor Company

- Modified Support Materials
  - Use novel, high surface area, layered oxides as precious metal supports
- Cost and Performance Models
  - Estimate finished catalyst costs; predict vehicle tailpipe performance.

Oak Ridge National Laboratory

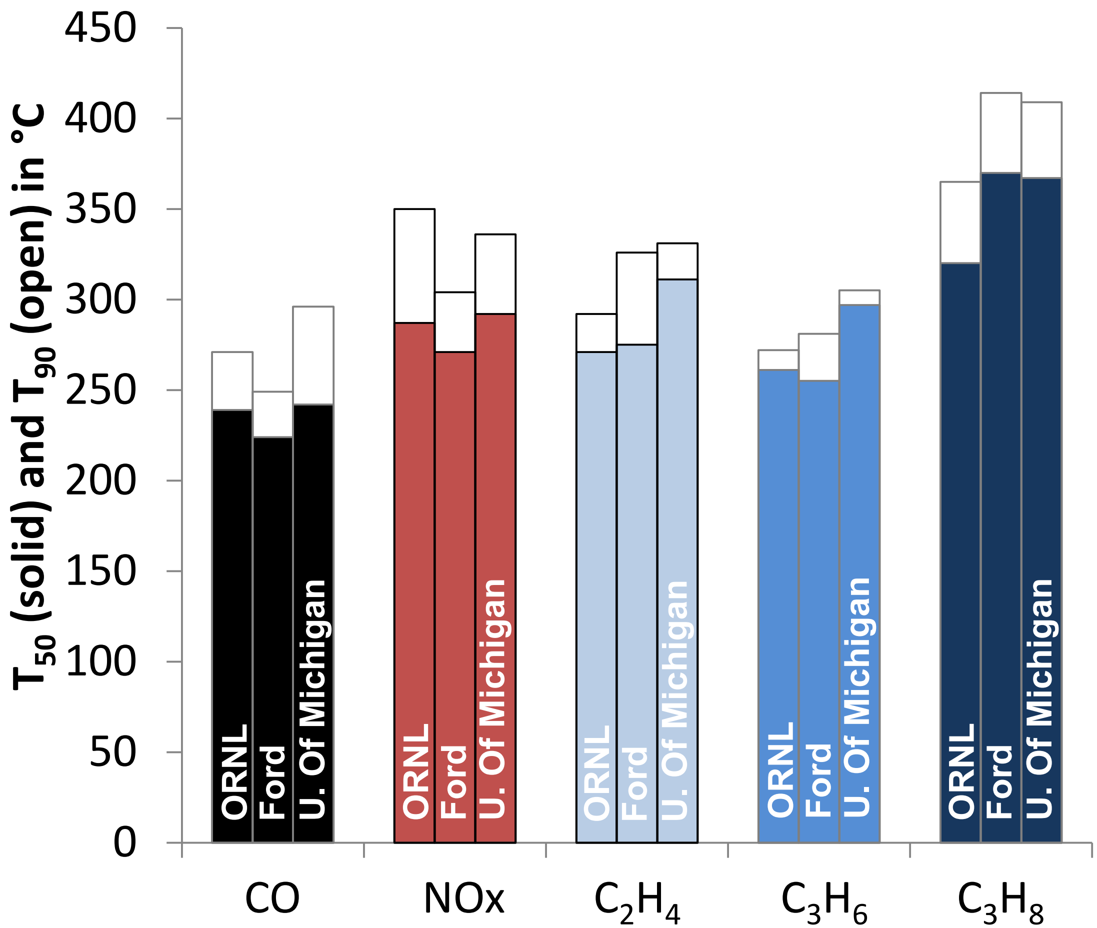
- Modified Support Materials
  - Investigate modification of supports for thermal stability, adherence of metal to the support, and tailoring the metal-support interactions for optimal catalytic performance.
- Ternary Oxide Development as PGM Substitute
  - Investigate the functionality of low-PGM or PGM-free, ternary-oxide catalyst systems, starting with CuO-CoO-CeO (CCC).

University of Michigan

- Core-Shell Model Catalysts (incl. monolith cores)
  - Investigate catalyst architectures containing a core-shell conformation composed of a metal nanoparticle surrounded by a metal oxide shell.
  - Synthesis will begin with silica, alumina, and ceria-zirconia-based model catalyst systems

"Round Robin" confirmed reactor similarities with aged modern TWC

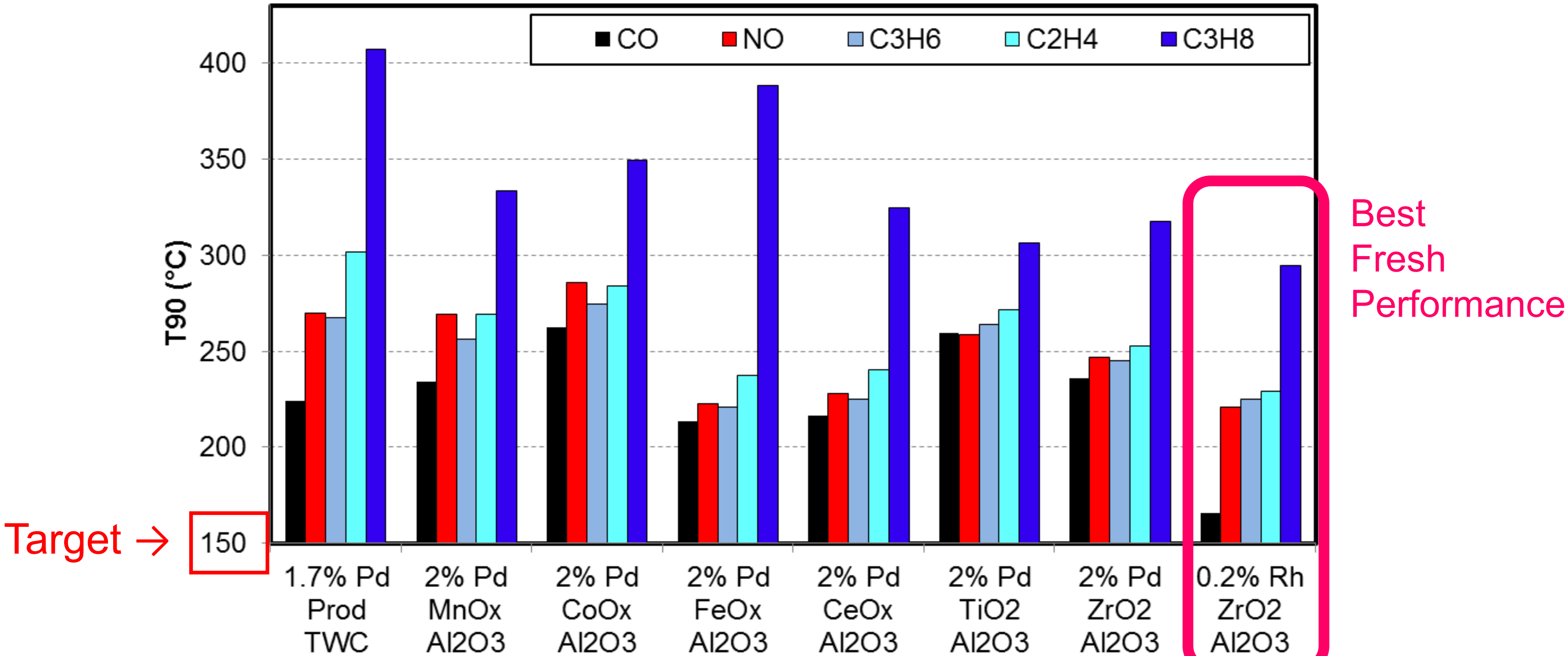
- TWC aged by Ford
  - 50h 4-mode durability
  - 960°C max bed temperature
- Evaluated at all partner organizations using protocol developed by ACEC tech team
- Good agreement at each research lab even though sample weights range from 0.1 to 2.0 g



ACEC stoich protocol:

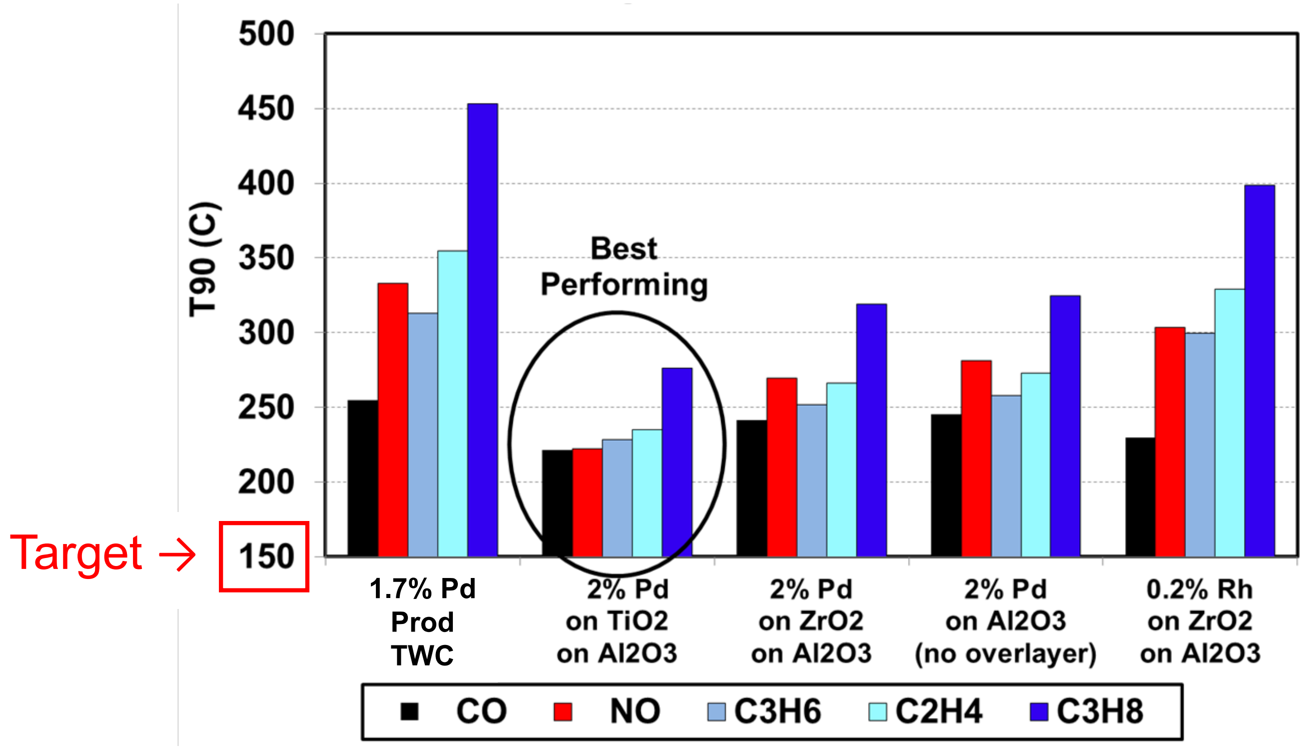
$[H_2O]$ = 10%	$[O_2]$ = {stoichiometric}	$[CO_2]$ = 5%	[NO] = 1000ppm
[CO] = 5000ppm	$[C_3H_8]$ = 150ppm	$[C_3H_6]$ = 500ppm	$[C_2H_4]$ = 525ppm
$[H_2]$ = 1700ppm	N_2 or Ar Balance	0.2 – 3.4 slm flow	0.1 – 2.0 g crushed monolith

Performance of Catalysts in the Fresh State



- **Fresh production TWC does not satisfy the T90 target of 150˚C for any exhaust gas**
- **Some of the overlayers with 2% Pd outperformed the production TWC**
- **The Rh on ZrO_2 overlayer had the best fresh performance**
  - **Fresh CO T90 near program target**

Performance After 950°C Oven Aging in Air/H_2O

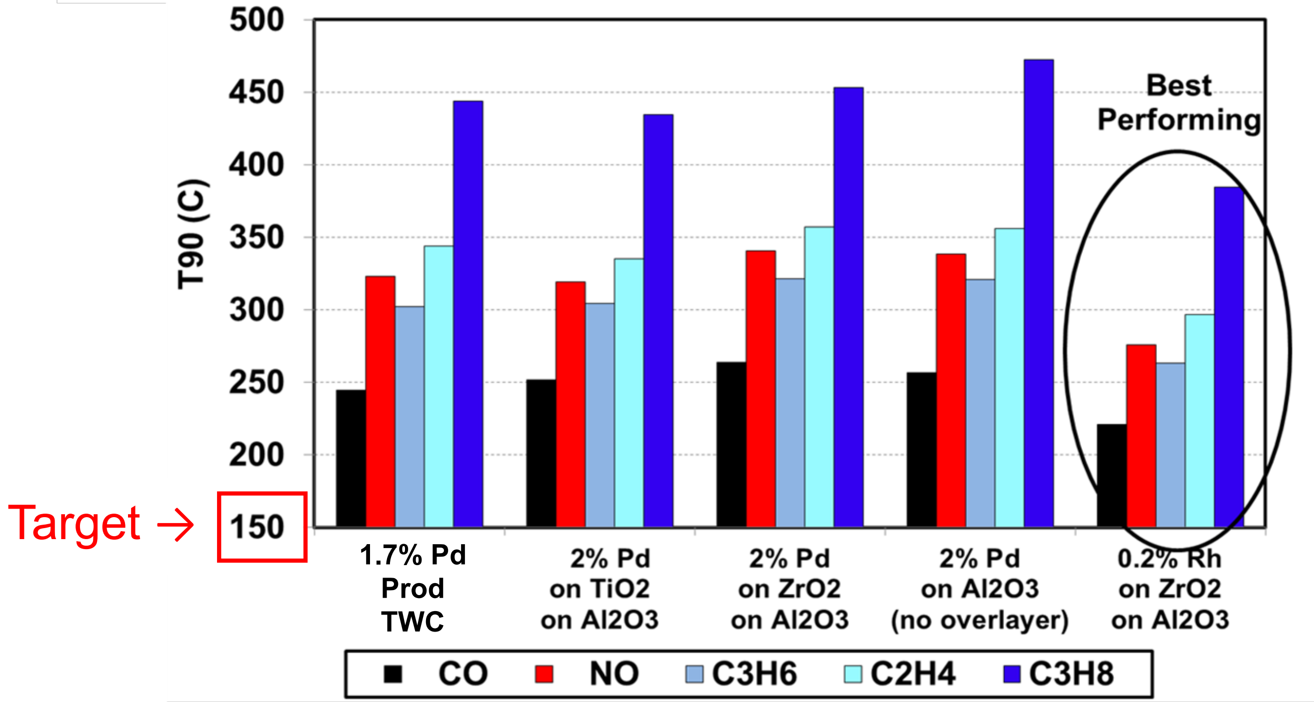


- **All of the over-layer formulations had better performance than the production TWC after lean aging at 950°C**
- **The 2% Pd on TiO_2 overlayer provided the best performance**
  - **Performance *improves* after lean aging!**

Accomplishments

Research and Advanced Engineering

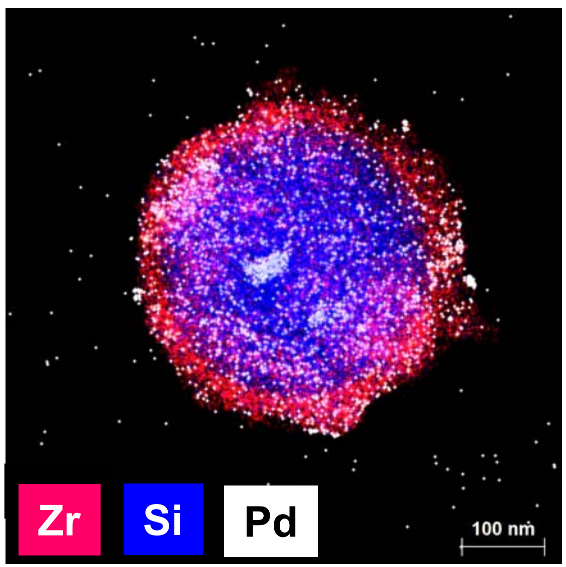
Catalyst Results After 4-Mode Aging 960°C max



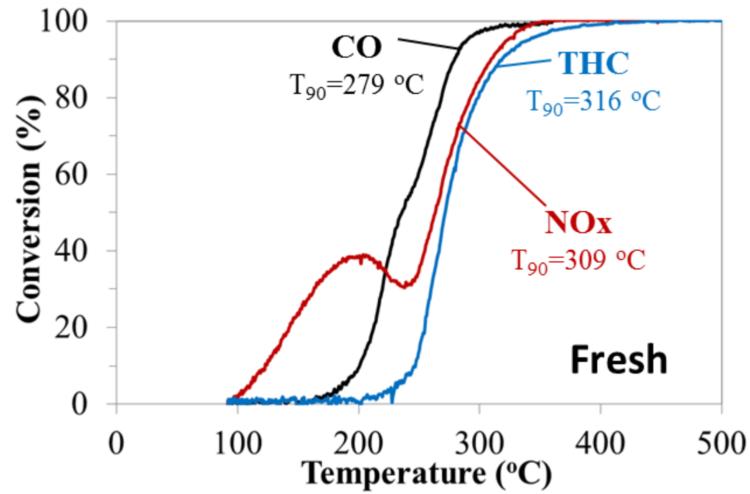
- **After 4-mode aging, the 0.2% Rh on Zr over-layer provided the best performance**
- **Lean aging not appropriate for catalysts intended primarily for stoichiometric operation**

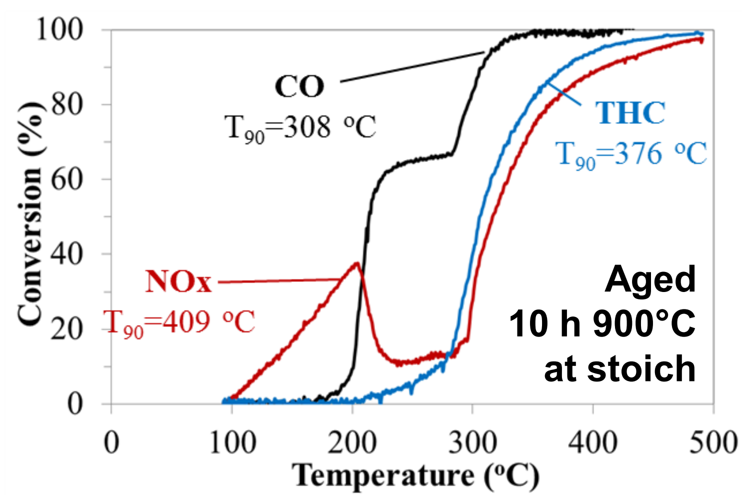
Goal: Improve ZrO_2 surface area through deposition on SiO_2 core

- Previous lean data suggested Pd/ZrO_2 was promising
- Coat a SiO_2 with ZrO_2 shell then add 1% Pd
- Pd particles are on ZrO_2 shell, but initial deposition has poor dispersion → improvements underway



Elemental maps while rotating a fresh sample ±40° (TEM).





This research was performed, in part, using instrumentation provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program, and the Nuclear Science User Facilities

Accomplishments

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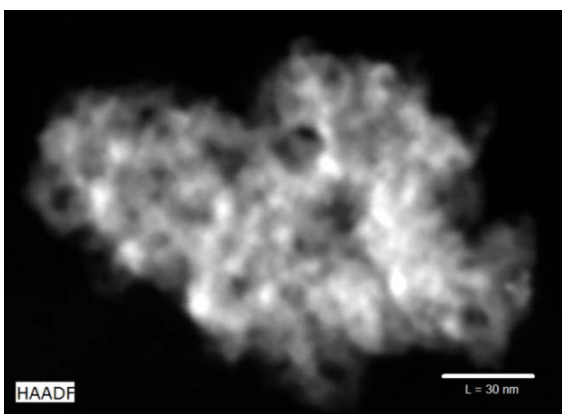
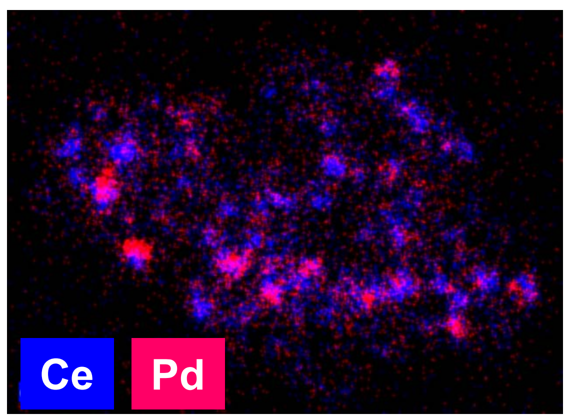
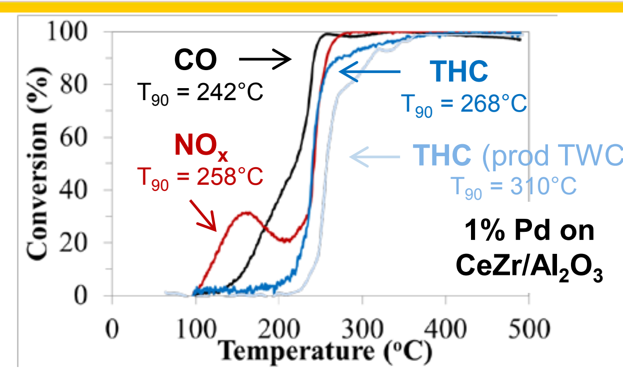
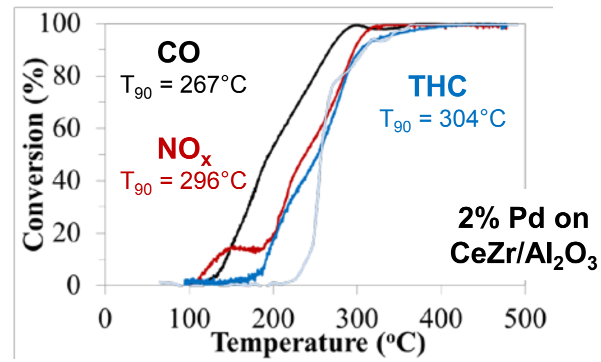
Enhanced activity through deposition of well defined nanoparticles of Ce-Zr with targeted deposition of Pd

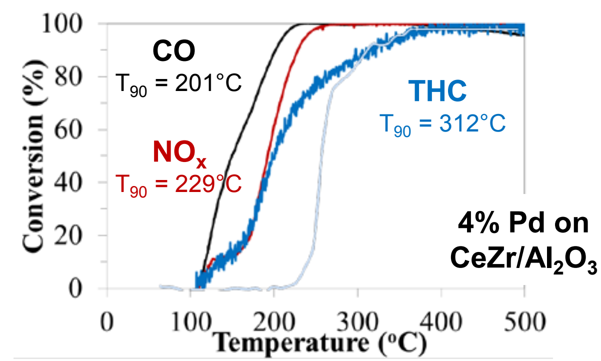
- Dispersion of Ce-Zr nanoparticles on Al_2O_3
- Target deposition of Pd on nanoparticles on Ce-Zr
  - TEM used to confirm both nanoparticles and targeted deposition











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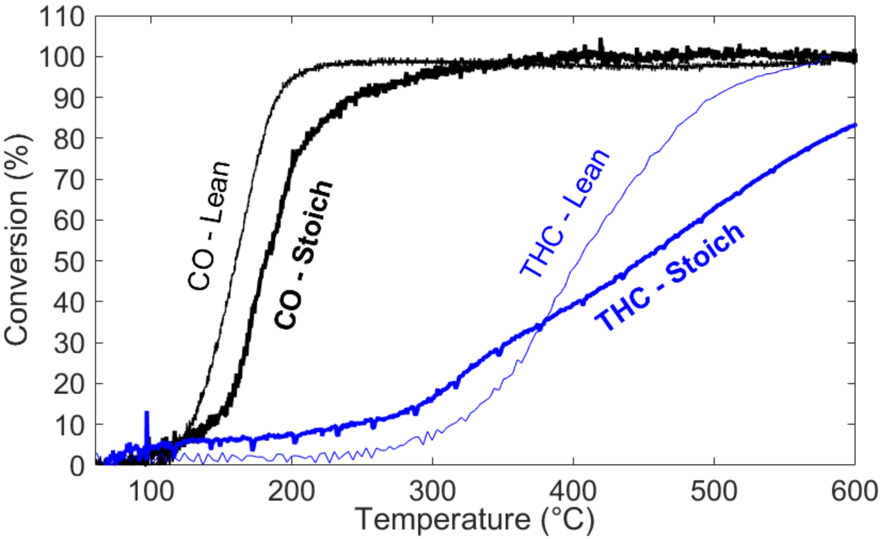
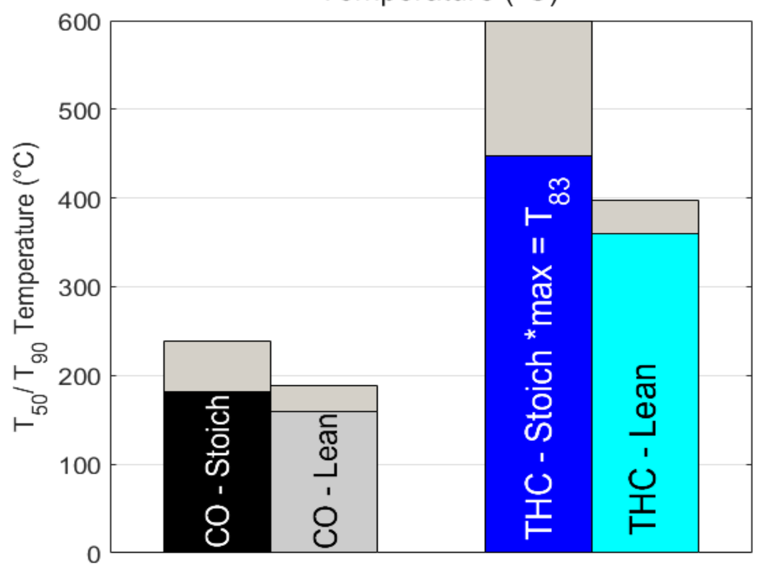
Ternary Oxide as PGM substitute shows promise, but only for CO

- CuO-Co_3O_4-CeO_2 (CCC) catalyst has shown inhibition resistance for lean CO oxidation
- Also a good CO oxidation catalyst under stoichiometric conditions
- CCC is clearly poor for HC and NO and can only be considered as a "specialist" for CO

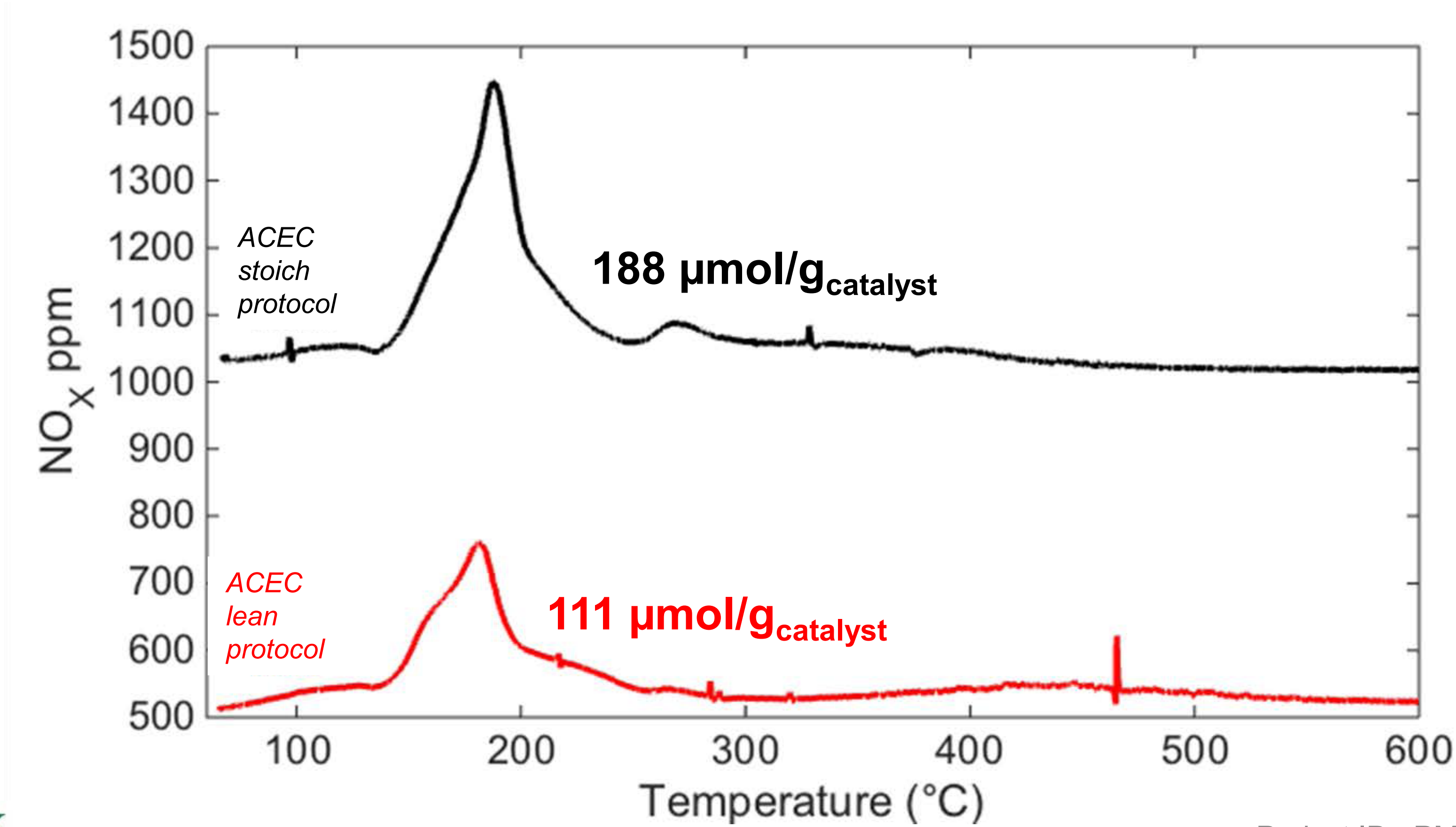
Continuing work

- CCC catalyst as a CO oxidation "specialist"; use less PGM in system
- New Formulations:
  - Increase surface area, Cu content, and Cu-Ce interface active site
  - Improve the already good CO oxidation activity



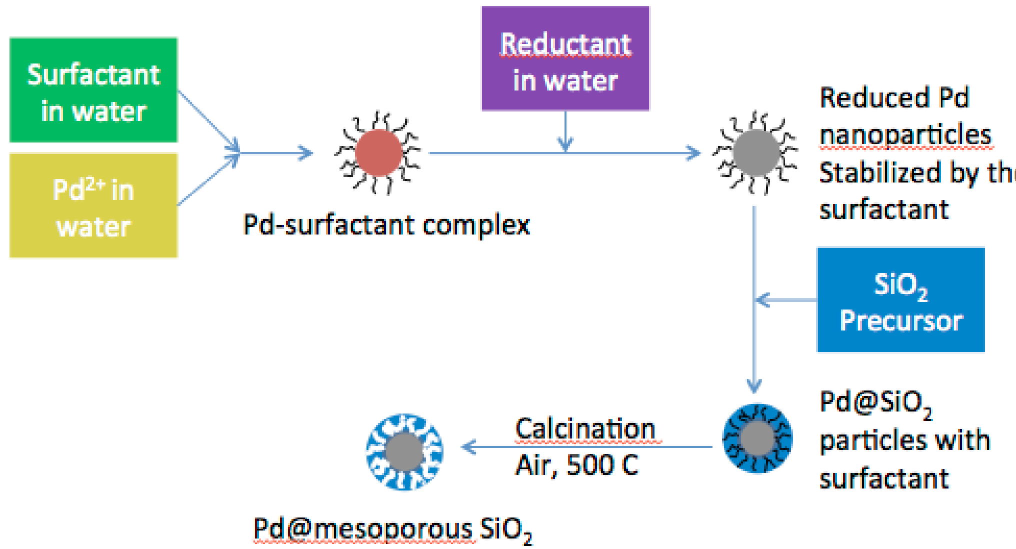


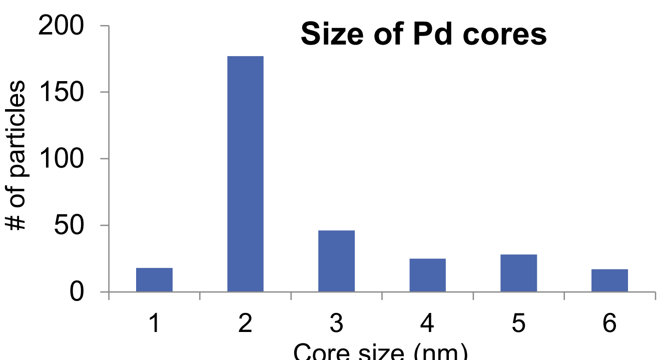
CCC also shows the ability to store and release NOx at low temperatures

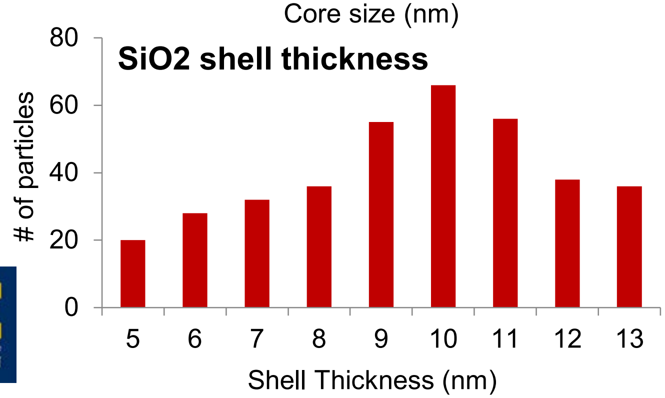


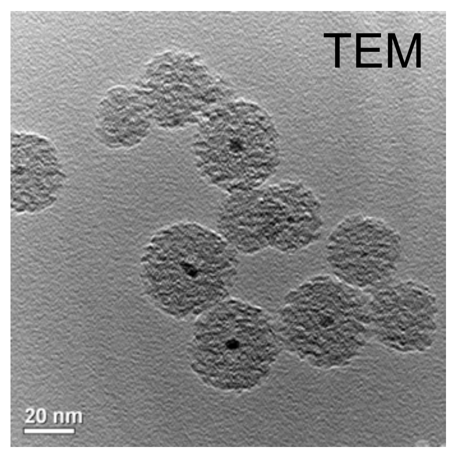
One-Pot Synthesis of $Pd@SiO_2$ Core@Shell Catalyst

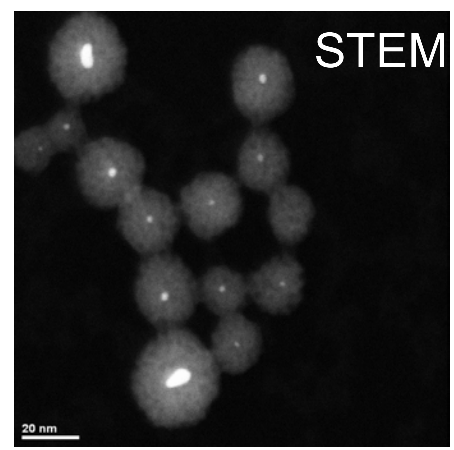
1) Core@shell by flame spray pyrolysis
2) Simple 1-pot synthesis of core@shell
3) Now being extended to other shell oxides (e.g., $Pd@TiO_2$, $Pd@SiO_2$-CeO_2)











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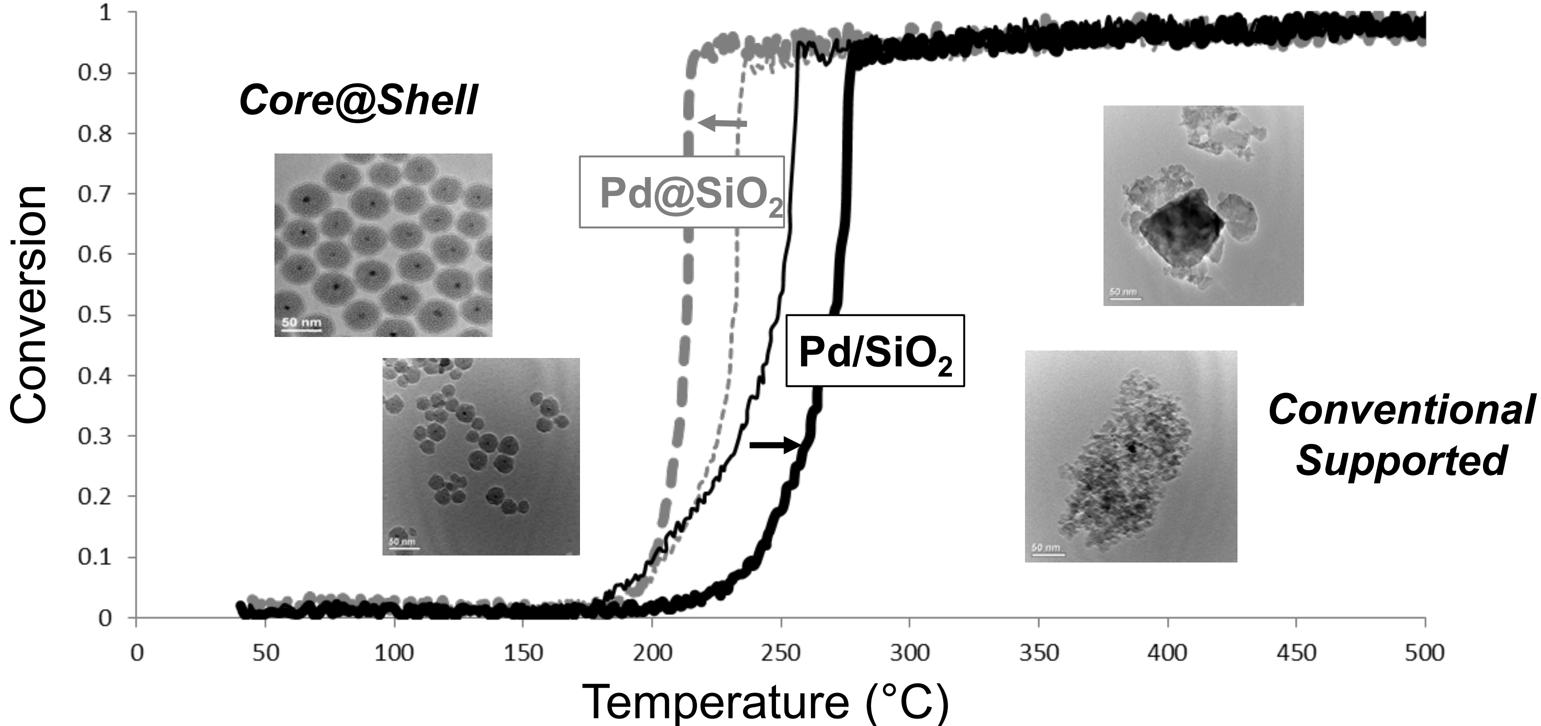
Activity Comparison by CO Oxidation Probe Reaction

- Feed: 1% CO, 1.5% O_2, balance N_2, 400ml/min flow, 60 mg sample
  - Fresh (thin lines) and aged (thick lines) at 850°C for 4 h in dry air



- **New synthesis route leads to thermally stable $Pd@SiO_2$ core shell catalyst**
- **$Pd@SiO_2$ is better dispersed after aging at 850°C**
- **$Pd@SiO_2$ shows improved light-off behavior after aging at 850°C**

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Accomplishments

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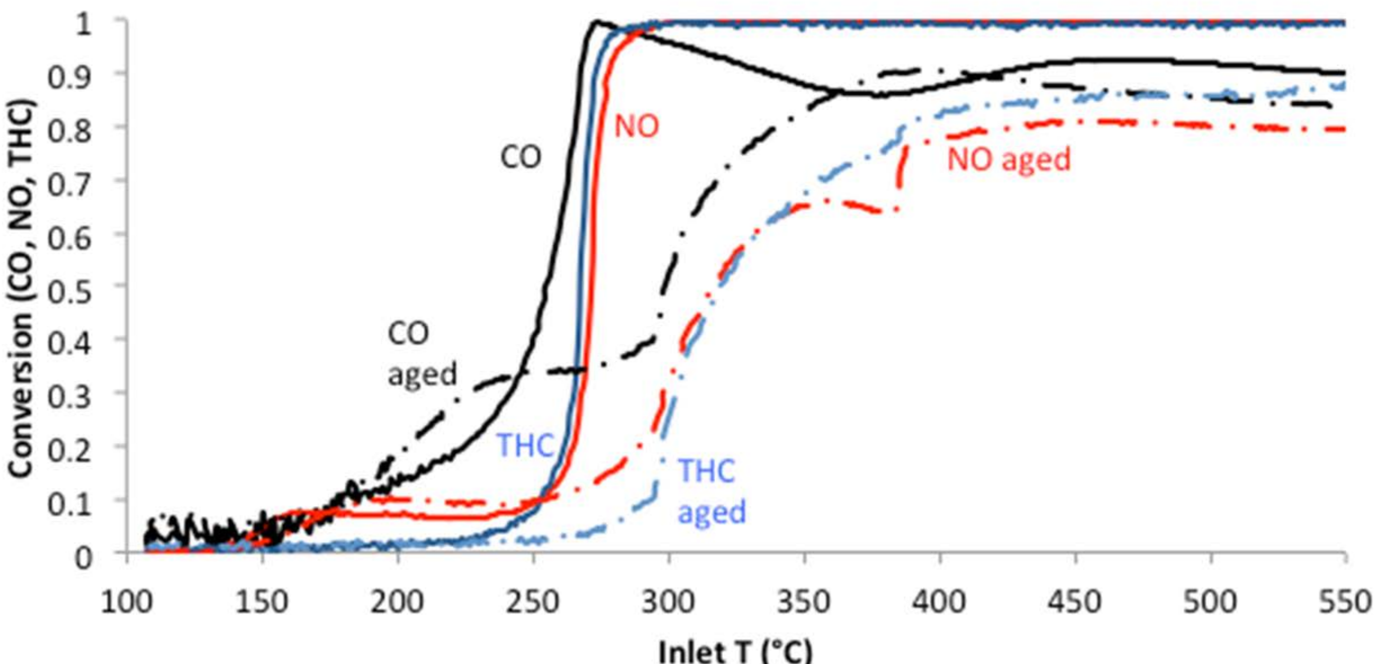
Test Results for Hydrothermally Aged Pd@SiO_2 Core@Shell Catalysts



Feed: Full mix, 212 ml/min total, 5% water; 60 mg fresh Pd@SiO_2 (solid line); 60 mg aged Pd@SiO_2 (dotted line); aging in air at 800°C for 10 h with 6% water

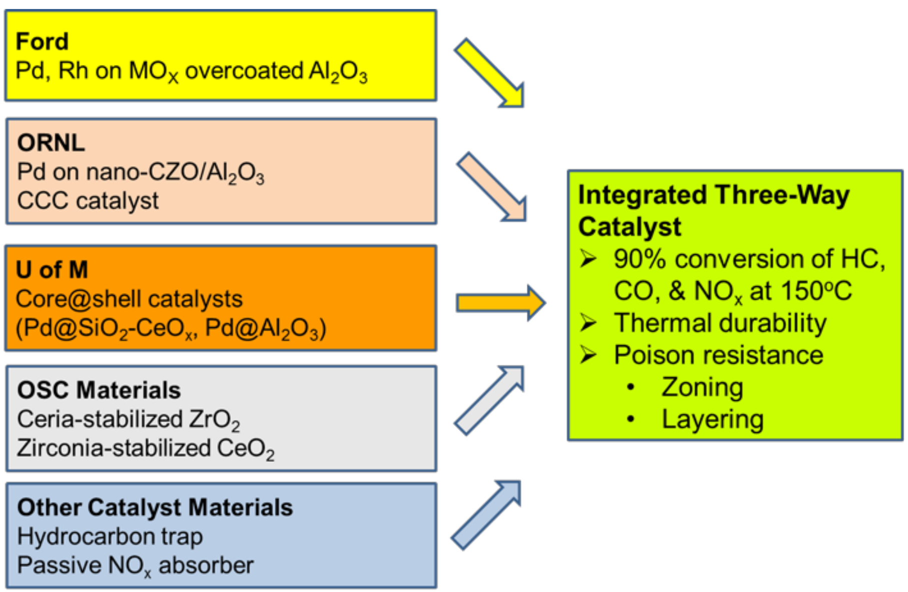
- **Simple one-pot synthesis for Pd@SiO_2 core-shell catalyst has been developed**
- **Core-shell catalyst shows better activity than supported Pd/SiO_2 catalyst**
- **Pd@Al_2O_3 and Pd@CZO will be more hydrothermally durable**

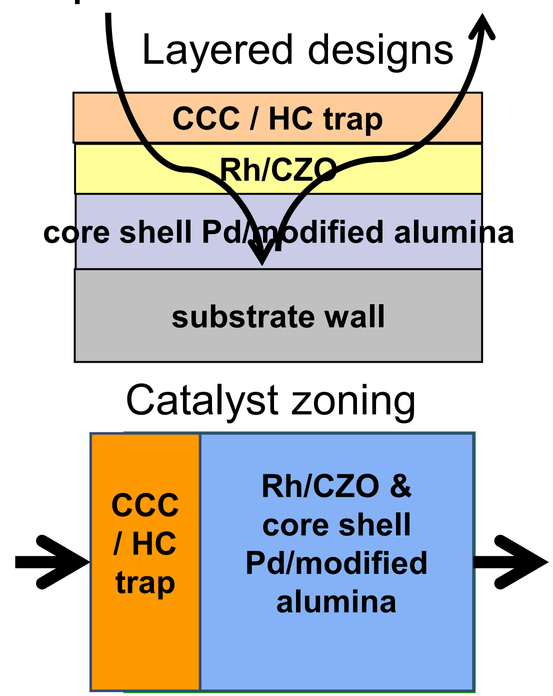
Remaining Challenges and Barriers

- Long lead times for materials commercialization
  - Use materials with known, high stability in automotive exhaust
  - Use commercially available support materials as a base and add new materials onto base to support metals in novel ways
  - Combine novel materials into a complete catalyst
  - Partner with major automotive catalyst supplier in third year
- Cost
  - Develop stable, high surface areas for better metal dispersion
  - Balance PGM within system to take advantage of lower costs when possible
  - Investigate base metals as PGM substitute
  - Fewer processing steps are desirable

Proposed Future Work

- Identify and capitalize on synergies between various catalyst materials
- Demonstrate full aging (hydrothermal-chemical) and performance from coated monolith cores using most promising materials
- Identify system solutions and estimate vehicle performance and cost





Response to Previous Year's Comments

- This project has not been previously reviewed

Summary

Ford Research and Advanced Engineering

- Relevance: TWC materials required to be active at lower temperatures to satisfy strict emission standards with the next generation of automobiles
- Approach: Make and characterize new materials, and predict performance and costs; leverage cross-laboratory analytical capabilities
- Collaboration: Full collaboration between Ford, UM, and ORNL
- Technical Accomplishments
  - Commercial TWC "round robin" was used to demonstrate reactor-to-reactor compatibility amongst all three partners
  - Overlayers of metal oxides on high surface area alumina successfully resulted in equal or better TW performance in aged state, most notably $Pd/TiO_2/Al_2O_3$ and $Rh/ZrO_2/Al_2O_3$
  - Pd on zirconia shell and ceria-zirconia nanoparticles showed some promise; more work needed
  - Ternary base metal oxides = "CO specialist"; also stores NOx at low temperatures
  - Successful demonstration of one-step core@shell synthesis; pursuing additional shell materials with improved stability during aging
- Future work: continue towards shorter lead times for materials commercialization and lower costs

Technical Backup

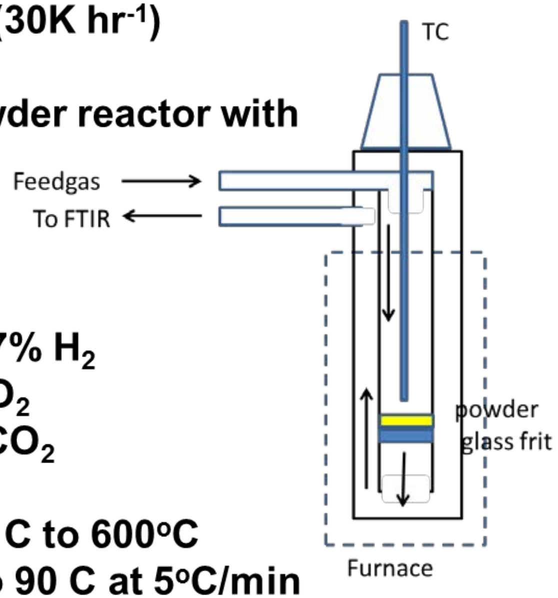
ACEC Test Protocols

1 gram of powder

3.6 L/min of flow (30K hr^{-1})

Evaluated on powder reactor with
- 525 ppm C_2H_4
- 500 ppm C_3H_6
- 150 ppm C_3H_8
- 1000 ppm NO
- 0.5% CO + 0.17% H_2
- 0.69 to 0.74% O_2
- 10% H_2O and CO_2

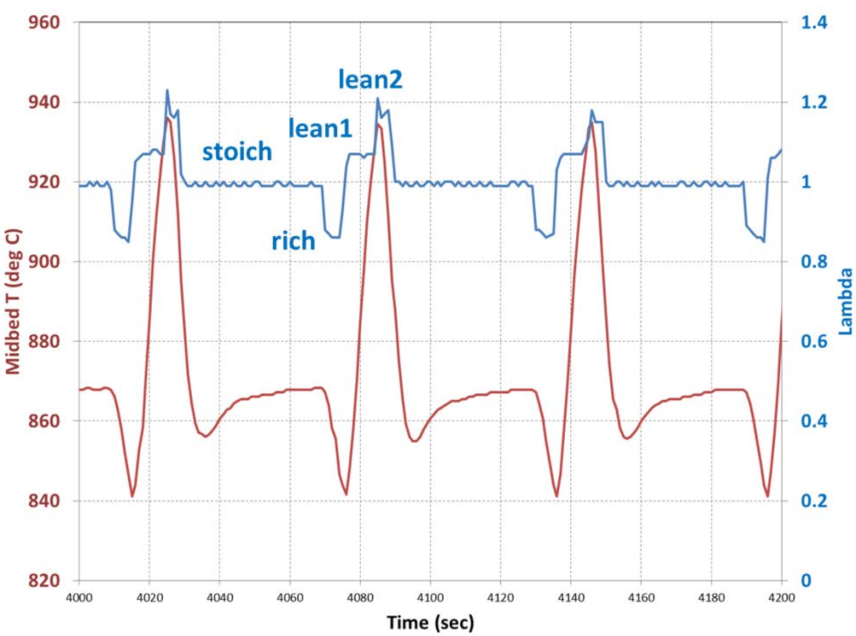
Ramp up from 70 C to 600°C and back down to 90 C at 5°C/min



Inlet TC recorded and used for control

Four Mode Aging Cycle

Repeated on pulsating flame combustor for 50 h



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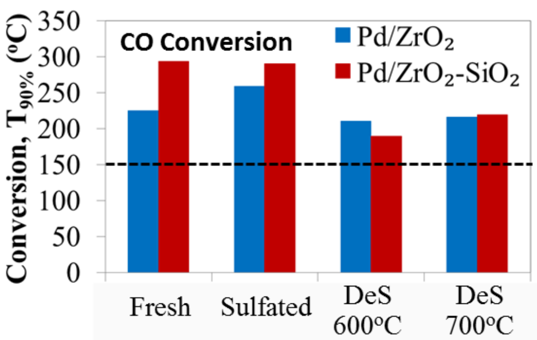
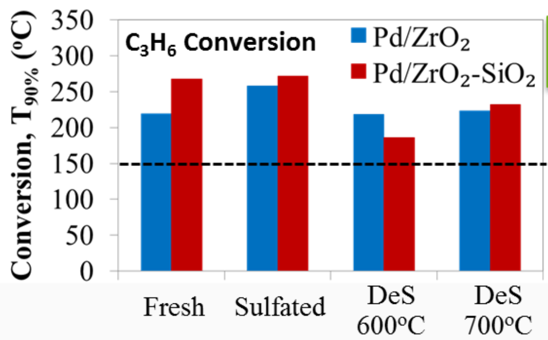
Synthesis of Layered Oxide Supported Catalysts

Lean-based study is motivation of new synthesis of SiO_2@ZrO_2 core@shell improves ZrO_2 coverage of SiO_2

- **Approach: optimize support for Pd catalysts by combining high acidity of ZrO_2 with high surface area of SiO_2; coated SiO_2 with ZrO_2**
- **ZrO_2 coating introduces surface acidity**
  - High acidity: benefit on HC oxidation vs. high basicity: high sulfur adsorption
  - Pd/ZrO_2 has both strong acidic and basic sites, while Pt/Si has neither

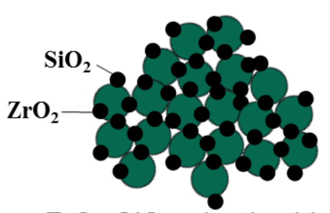




Pd/ZrO_2 outperforms Pd/ZrO_2-SiO_2 in most cases

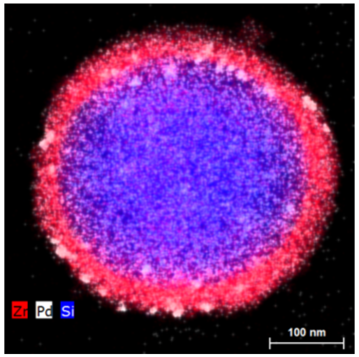
Reaction Conditions: 4000 ppm CO, 500 ppm NO, 1000 ppm C_3H_6, 4% O_2, 5% H_2O in Ar, Total Flow: 200 sccm

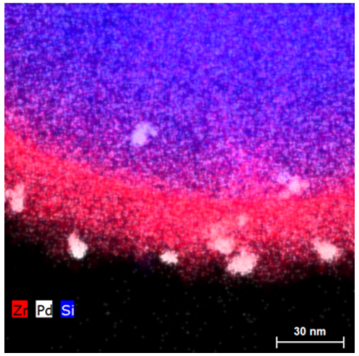
Improved zirconia adherence+dispersion necessary



ZrO_2-SiO_2 mixed oxide

New technique developed to form a monolayer shell of ZrO_2 on a SiO_2 core



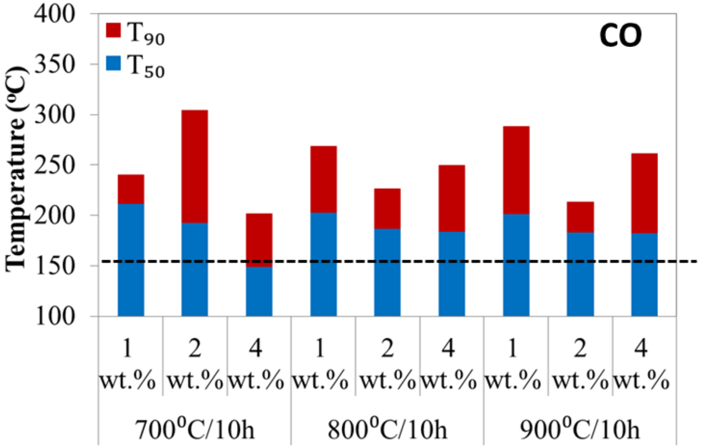


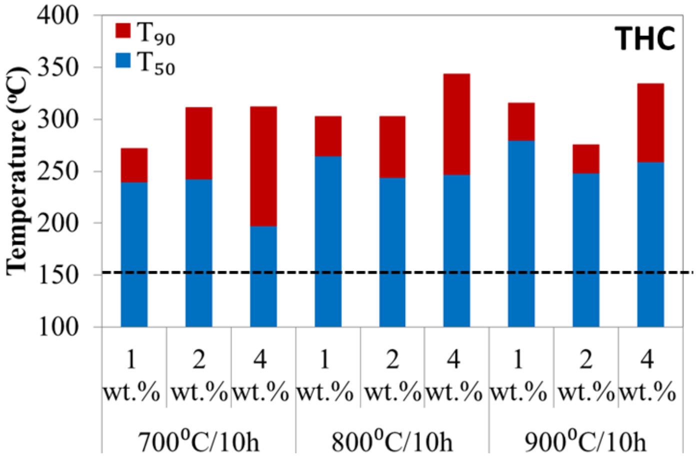
Improved CO and THC conversion over the 2 wt.% Pd/CeZr-Al_2O_3 catalysts after aging at 900°C for 10 hours

- 1 and 4 wt.% Pd/CeZr/Al_2O_3 catalysts deactivate after hydrothermal aging at 800 and 900 °C.
- **HT aging at 800°C:** improved performance of the 2 wt.% Pd/CeZr/Al_2O_3 catalyst for both CO and THC conversion.
- **HT aging at 900°C:** 2 wt.% Pd/CeZr/Al_2O_3 catalyst has the lowest $T_{50,90}$'s compared to the 1 and 4 wt.% Pd/CeZr/Al_2O_3, indicating that it is the most durable catalyst at elevated temperatures.

ACEC protocol (S-GDI)

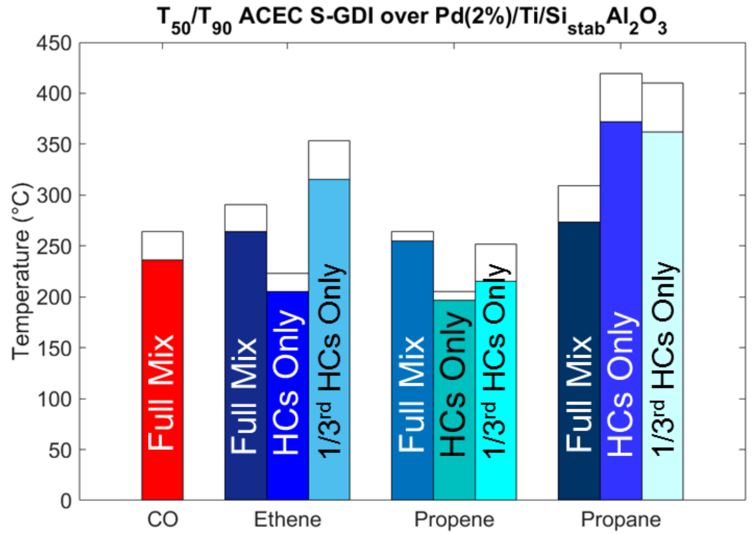
100 mg cat. / flow: 333 sccm /water bath: 60°C
CO_2:13%, O_2: Stoic – 0.05%, H_2O: 10%, CO:0.5%, NO:0.10%, H_2: 0.167%, C_2H_4: 0.0525%, C_3H_6: 0.05%, C_3H_8: 0.015%, Ar balance

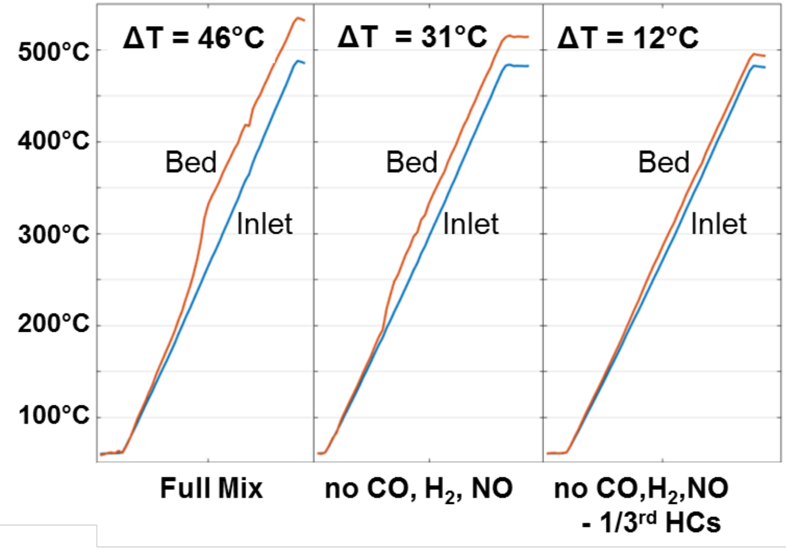




Exotherm Effects Significant

Sequential tests were conducted to determine the effect of varying exotherm and conditions on overall performance.





The streams were: Full S-GDI Mixture, S-GDI (CO and NO removed), and S-GDI (CO and NO removed, 1/3rd Hydrocarbons by ppm). Results:

- CO and NO are a significant inhibitor to Ethene and Propene performance – Performance increased significantly with the removal of CO.
- Exothermic effects can drastically increase Ethene and Propene performance – Performance decreased with the removal of 2/3rd hydrocarbons and subsequent loss of exotherm.